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(54) **Colorless petroleum marker dyes**

(57) A composition comprising a liquid petroleum product and a colorless marker compound in an amount that is not detectable visually, and a method for marking a liquid petroleum product with a colorless marker compound.

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Description

Background

[0001] This invention relates generally to a composition comprising a colorless marker dye and a liquid petroleum product, and to a method for marking petroleum products.

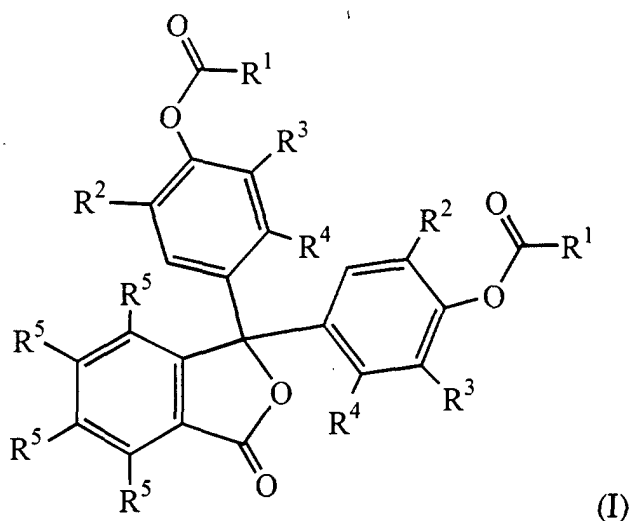
[0002] Certain phthalein derivatives are known and used as markers in petroleum applications and other industrial applications such as paints and plastics. For example, U.S. Pat. No. 6,002,056 describes the use of thymolphthalein, cresolphthalein and related compounds as markers for petroleum products. However, this reference discloses only compounds having two phenolic hydroxyl groups, and does not suggest the use of phthalein esters as markers.

[0003] The disadvantages of phthalein derivatives stem from their typically low solubility in petroleum products. As a result of this characteristic, phthalein markers can be removed from a marked petroleum product by extraction with water, either deliberately by one seeking to circumvent the marking, or as a result of contact of the marked petroleum product with water bottoms in storage tanks.

[0004] The problem addressed by this invention is to find colorless marker dyes with improved solubility in petroleum products.

Statement of Invention

[0005] The present invention is directed to a composition comprising a liquid petroleum product and a compound of formula I in an amount that is not detectable visually.



In formula I, R^1 is C_1 - C_{18} alkyl, C_1 - C_{18} alkenyl, aryl or aralkyl; R^2 , R^3 and R^4 are independently hydrogen, C_1 - C_{12} alkyl, chloro or bromo; and R^5 is hydrogen, chloro or bromo.

[0006] The present invention is further directed to a method of marking a liquid petroleum product comprising adding to the petroleum product as a marker an amount of a compound of formula I that is not detectable visually, and wherein the marker develops a color on contact with a developing reagent.

Detailed Description

[0007] An "alkyl" group is a hydrocarbonyl group having from one to eighteen carbon atoms in a linear, branched or cyclic arrangement. Substitution on alkyl groups of one or more halo, alkoxy, alkanoyl or amido groups is permitted; alkoxy, alkanoyl and amido groups may in turn be substituted by one or more halo substituents. Preferably, alkyl groups are unsubstituted. An "alkenyl" group is an "alkyl" group in which at least one single bond has been replaced with a double bond. An "aryl" group is a substituent derived from an aromatic compound, including heterocyclic aromatic compounds having heteroatoms chosen from among nitrogen, oxygen and sulfur. An aryl group has a total of from five to twenty ring atoms, and has one or more rings which are separate or fused. Substitution on aryl groups of one or more halo, alkyl, alkenyl, alkoxy, alkanoyl or amido groups is permitted, with substitution by one or more halo groups being possible on alkyl, alkenyl, alkoxy, alkanoyl or amido groups. Preferably, aryl groups are unsubstituted or are

substituted only by halo or alkyl groups. An "aralkyl" group is an "alkyl" group substituted by an "aryl" group.

[0008] It is preferred that R^2 , R^3 and R^4 are hydrogen or alkyl having from one to four carbon atoms. It is also preferred that R^1 is alkyl having from one to four carbon atoms. It is preferred that R^5 is hydrogen.

[0009] It is preferred that the liquid petroleum product is gasoline, diesel fuel, jet fuel, fuel oil, kerosene or lamp oil. It is preferred that the compound of formula I is present in an amount from 0.5 ppm to 100 ppm, and further preferred that it is present in an amount from 0.5 ppm to 10 ppm. It is preferred that the compound of formula I is prepared as a mixture with a high-boiling hydrocarbon-soluble solvent. Preferred solvents include 1-octyl-2-pyrrolidone, mixed methylnaphthalenes (sold as AROMATIC 200 by Exxon Corporation) or aromatic hydrocarbon solvents. The preferred concentration of the marker in the solvent is from 20% to 30%.

[0010] The developing reagent is a strongly basic reagent, e.g., a hydroxide of an alkali metal or of a quaternary ammonium ion. Preferably, the reagent is a quaternary ammonium hydroxide.

[0011] This invention is further directed to the compound of formula I in which R^1 is propyl, R^2 is methyl, and R^3 , R^4 , and R^5 are hydrogen. Preparation of this compound is described in Example 1.

Examples

Example 1: Preparation of the Di-n-Butyl Ester of o-Cresolphthalein

[0012] To a 100 mL, three-neck round-bottom flask fitted with a stirrer, thermocouple and a condenser, the following raw materials were added: (1) o-cresolphthalein, 1.73 g (0.005 moles); (2) water, 30 mL; (3) 50% NaOH, 0.8 g; (4) Na_2CO_3 , 0.6 g; and (5) xylenes, 8 g. The mixture was stirred at 20-25°C for one hour, during which butyric anhydride, 2 g, was added. The mixture was then heated to 50-55°C until TLC revealed that the esterification reaction was complete. The upper xylenes layer was separated and 1-octyl-2-pyrrolidone, 2.5 g was added to it. Xylenes and water were removed azeotropically under vacuum. A residue of 6.6 g was obtained.

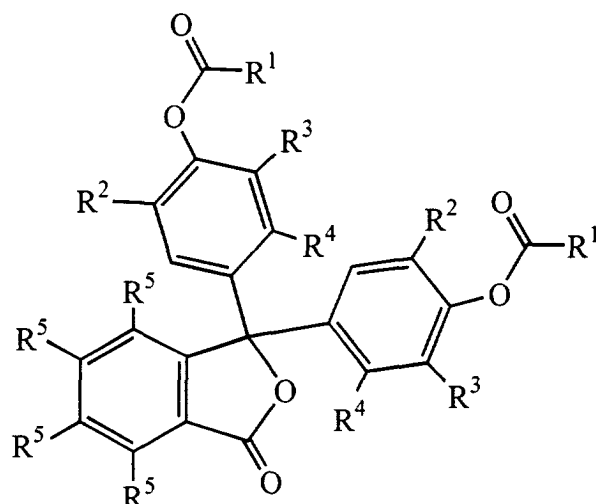
[0013] A marker solution was prepared by dissolving a 100 mg portion of the residue in xylenes (100 mL), and diluting 1 mL of the resulting solution to 100 mL with kerosene to make a 10 ppm solution.

[0014] A developer was made by dissolving 1g of a 40% solution of benzyltrimethylammonium hydroxide in methanol in 99 g of 2-ethyl-1-hexanol. To a 10 mL portion of the 10 ppm marker solution prepared above was added 2.5 mL of the developer. After the mixture was shaken for a few seconds, it acquired a blue-purple color. If necessary, quantitative determination of the marker concentration can be accomplished by measuring the absorbance of the solution at a wavelength of 581 nm.

[0015] A 10 mL portion of the 10 ppm solution prepared above was stirred with 10 mL of water for ½ hour and the layers were separated. To the organic layer was added 2 mL of the developer solution, resulting in development of a blue-purple color. Addition of 2 mL of developer solution to the water layer gave no color. This indicated that the marker was not extracted into the water layer.

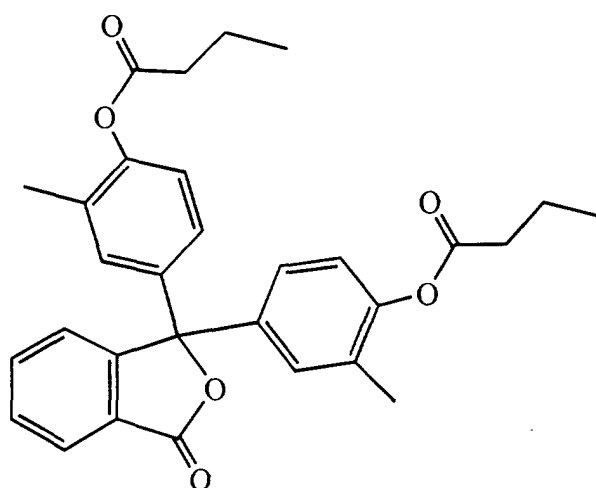
Claims

1. A composition comprising a liquid petroleum product and a compound having the formula

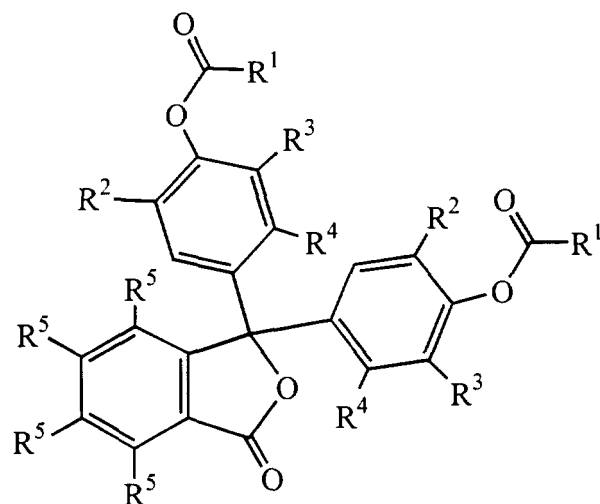


wherein R^1 is C_1 - C_{18} alkyl, C_1 - C_{18} alkenyl, aryl or aralkyl; R^2 , R^3 and R^4 are independently hydrogen, C_1 - C_{12} alkyl, chloro or bromo; and R^5 is hydrogen, chloro or bromo; and wherein said compound is present in an amount that is not detectable visually.

2. The composition of claim 1 in which said compound is present in an amount from 0.5 ppm to 100 ppm.
3. The composition of claim 2 in which said liquid petroleum product is gasoline, diesel fuel, jet fuel, fuel oil, kerosene or lamp oil.
4. The composition of claim 3 in which R^2 , R^3 and R^4 are hydrogen or alkyl having from one to four carbon atoms.
5. The composition of claim 4 in which R^1 is alkyl having from one to four carbon atoms and R^5 is hydrogen.
6. A compound having the formula



7. A method of marking a liquid petroleum product comprising adding to the petroleum product as a marker a compound of formula



wherein R^1 is C_1 - C_{18} alkyl, C_1 - C_{18} alkenyl, aryl or aralkyl; R^2 , R^3 and R^4 are independently hydrogen, C_1 - C_{12} alkyl, chloro or bromo; and R^5 is hydrogen, chloro or bromo; wherein the compound is not detectable visually, and wherein the compound develops a color on contact with a developing reagent.

8. The method of claim 7 in which said compound is present in an amount from 0.5 ppm to 100 ppm.
9. The method of claim 8 in which said liquid petroleum product is gasoline, diesel fuel, jet fuel, fuel oil, kerosene or lamp oil.
10. The method of claim 9 in which R^2 , R^3 and R^4 are hydrogen or alkyl having from one to four carbon atoms, R^1 is alkyl having from one to four carbon atoms and R^5 is hydrogen.